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# ATOMIC EMISSION SPECTROSCOPY METHODS FOR MEASUREMENT OF IMPURITIES IN URANIUM

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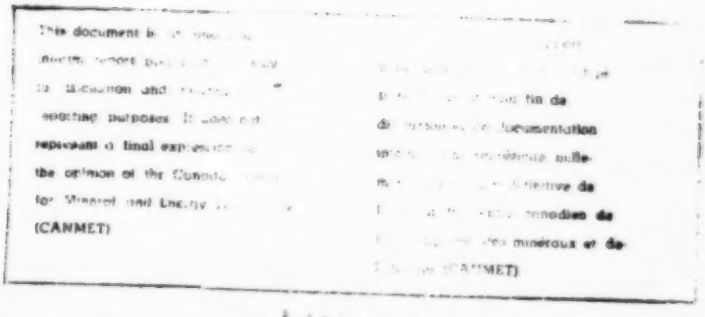

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# ATOMIC EMISSION SPECTROSCOPY METHODS FOR MEASUREMENT OF IMPURITIES IN URANIUM

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## ABSTRACT

The Division of Nuclear Fuel Cycle of the International Atomic Energy Agency requested the participation of CANMET in the preparation of a manual of analytical methods for the uranium industry. The staff of the chemical laboratory has responded to this request and will issue several reports describing current methodology and laboratory practice. This report deals with the determination of impurities, at the parts per million level, in uranium by three emission spectroscopic techniques.

Keywords: Uranium (impurities in)
Emission Spectroscopy
Inductively Coupled Plasma Analysis

# SPECTROSCOPIE D'ÉMISSION ATOMIQUE POUR MESURER LES IMPURETÉS DANS L'URANIUM

par

T.R. Churchill et R.E. Horton

## RÉSUMÉ

La division du cycle de combustible nucléaire de l'Agence internationale de l'énergie atomique a demandé que CANMET participe à la préparation d'un manuel des méthodes analytiques à l'intention de l'industrie de l'uranium. Le personnel du laboratoire de chimie a accepté et diffusera plusieurs rapports décrivant la méthodologie actuelle et les pratiques de laboratoire. Le présent rapport traite de la détermination des impuretés dans l'uranium (parties par million) à l'aide de trois techniques de spectroscopie d'émission.

# ATOMIC EMISSION SPECTROSCOPY METHODS FOR MEASUREMENT OF IMPURITIES IN URANIUM

Atomic emission spectroscopy methods of analysis suffer limitations when samples with high uranium concentrations are analyzed. These problems arise because the plethora of uranium wavelengths emitted can result in spectral interferences. Chemical interferences can also occur depending on the method of excitation. If Inductively Coupled Argon Plasma excitation is used the problem of chemical interference is virtually eliminated but the spectral interferences remain and in fact can be more severe. Spectral overlap can be minimized if a high resolution spectrometer is employed or if an Inductively Coupled Plasma Mass spectrometer instrument is used. Alternatively both the spectral and chemical interference problems can be reduced by using a pre-treatment procedure to separate the uranium from the analytes.

Two methods for the effective removal of uranium from the analytes are described: one is a solvent extraction method for use with solution samples which are then measured with an Inductively Coupled Plasma spectrometer, the other method for use with solid samples employs a carrier distillation technique with d-c arc excitation. A third method is described for measurement of impurities in uranium process solutions without prior separation of the analytes using a high resolution spectrometer.

## SPECTROGRAPHIC ANALYSIS OF URANIUM OXIDE ($U_3O_8$) BY GALLIUM OXIDE CARRIER TECHNIQUE

The following procedure is a slightly condensed version of standard method E402 of the American Society for Testing and Materials (ASTM). The method is included in the ASTM publication Methods for Emission Spectrochemical Analysis sponsored by the ASTM committee E-2 on Emission Spectroscopy.

### Summary of Method

The as-received sample is ignited to $U_3O_8$. It is important that the sample be in the same physical oxide form as are the comparison standards.

The sample is mixed with pure gallium sesquioxide ($Ga_2O_3$) in the ratio of 98 parts $U_3O_8$ to 2 parts $Ga_2O_3$. If densitometric determinations are desired, the $Ga_2O_3$ used in the mixture contains 1% chromium or 1% cobalt by weight. The chromium or cobalt is used as an internal standard element in the spectrochemical analysis. The $U_3O_8$-$Ga_2O_3$ is placed in a special cupped electrode and excited in a d-c arc. Varying amounts of impurities either in vapour form or as solid particles are carried up into the arc steam, along with the vaporized $Ga_2O_3$. The spectrum is recorded on a photographic plate and the spectral lines are either visually compared with standard plates or photometrically measured and compared with synthetic standards prepared according to standard spectrochemical procedures.

## Equipment

For mixing the sample and carrier either a highly polished agate mortar and pestle, or a suitable small sample mechanical mixer can be used. A balance with capacity up to a few grams and capable of weighing to the nearest 0.1 mg accurately is required. The excitation source must be capable of providing a 14-A d-c arc (short circuit) and the excitation stand should be a conventional type with adjustable water cooled electrode holders. The spectrograph must provide pre-exposure and exposure timers, have a wavelength coverage from 225 to 865 nm, a reciprocal linear dispersion of at least 0.5 nm/mm and sufficient resolving power to separate cadmium 228.802 nm from arsenic 228.12 nm. Photographic processing equipment for developing, fixing, washing and drying is required and must be capable of providing constant and reproducible temperature of the solutions. To examine the photographic plates a comparator-microphotometer is required, as a comparator to provide sufficient magnification and facility to compare spectral line densities of the sample and a reference standard plate or film; as a microphotometer having a precision of 1.0% or better for transmittance values between 5 and 95%.

## Reagents and Materials

For the visual comparison analysis, use a 99.99% pure $Ga_2O_3$. For densitometric analysis except for chromium, use a mixture of 98.54 parts of $Ga_2O_3$ and 1.47 parts of chromium sesquioxide ($Cr_2O_3$). This is equivalent to 1% chromium in this mix or to 200 ppm in the final $U_3O_8$-$Ga_2O_3$ mixture. For

densitometric analysis except for cobalt, use a mixture of 98.53 parts of $Ga_2O_3$ and 1.47 part of cobalt oxide ($Co_2O_3$). This is equivalent to 1% cobalt in this mix or to 200 ppm cobalt in the final $U_3O_8$-$Ga_2O_3$ mixture. The anode, pedestal and the counter electrodes should be of the S-1, S-2 and C-1 types respectively. The graphite should be a high purity type with an average density near 1.86 g/cm$^3$ and a specific electrical resistance near $4.5 \times 10^{-4}$ ohm-in.

## Standards

Standards can be synthesized by adding the impurity elements to purified $U_3O_8$ and homogenizing. Impurites in a solid or powder form, preferably as oxides, may be blended with $U_3O_8$; impurities in solution may be added to $U_3O_8$ and the mixture dried, blended, and reignited; or the impurities and uranium may be combined in solution and reconverted to $U_3O_8$. The individual elements should grade in such a ratio as to facilitate visual comparisons, such a ratio as 10-5-2-1 covering the desired analytical range for each. No single standard should have a total concentration of impurities exceeding 2000 ppm. The bulk densities of the standards and the sample $U_3O_8$ should be as nearly identical as possible. Similar element responses should be obtained with $U_3O_8$ standards with similar bulk densities, regardless of the method used to make the standards. The sample and comparison standards should have the same physical oxide form and oxide preparation, if possible. Wherever possible an independent analytical method should be used to verify the established concentrations in the standards. The elements or compounds used to synthesize $U_3O_8$ standards should be of the highest purity.

## Preparation of Samples

Combine 980 mg of the $U_3O_8$ sample and 20 mg of the proper $Ga_2O_3$ carrier by thoroughly grinding with an agate mortar and pestle. Weigh quadruplicate 100 mg $U_3O_8$-$Ga_2O_3$ charges into anode electrodes held in a plastic electrode board. Gently tap the electrode board to settle the electrode charges. Compress the charges and introduce center vent hole in the charge with a venting tool.

Preparation of Apparatus

Insert a 3.18 mm counter electrode in the upper holder. Mount a 3.18 mm pedestal electrode so as to extend 12.7 mm above the lower electrode holder. Insert the anode electrode, with its charge, firmly on the pedestal. Adjust to an analytical gap of 4 mm., with its center aligned with the optical axis of the spectrograph. The sample is electrically positive. Produce and record the spectra in accordance with the following conditions:

Electrical Parameters

| | |
|---|---|
| Voltage | 250 V |
| Current | 14 A (short circuit) |

Exposure Conditions

1. General procedure for the following 26 Elements:
(Ag, Al, As, Au, B, Be, Bi, Cd, Co, Cr, Cu, Fe, Ge, In, Mg, Mn, Mo, Ni, P, Pb, Sb, Si, Sn, Tl, V, Zn)

| | |
|---|---|
| Spectral region, nm | 225 to 350 |
| Slit width, µm | 20 |
| Preburn period, s | 5 |
| Exposure period, s | 35 |

Step sector may be used to increase concentration ranges
Photographic emulsion, Eastman Kodak type SA-1 or equiv.

2. Ba, Li and Na:

| | |
|---|---|
| Spectral region, nm | 430 to 680 |
| Slit width, µm | 20 |
| Preburn period, s | 0 |
| Exposure period, s | 40 |
| Photographic emulsion Eastman Kodak | Type II-F |
| Filter, Corning No. | 3850 |

3. Cs, K, Rb:

| | |
|---|---|
| Spectral region, nm | 740 to 865 |
| Slit width, μm | 20 |
| Preburn period, s | 0 |
| Exposure period, s | 40 |
| Exposure emulsion Eastman Kodak | Type I-N |
| Filter, Corning No. | 3480 |

Make duplicate or quadruplicate exposures of each sample.

Photometry

1. Visual Comparative Analyses

Visually compare the density of the sample impurity spectral line with the corresponding line on a standard reference plate. Estimate the impurity concentration using the lines listed in Table 2. It is highly improbable that many of the 32 impurities will appear simultaneously in the 100 to 200 ppm concentration range. However, in most cases, the initial or alternate spectral lines designated will be free from spectral interference even when the other elements are near the maximum concentration indicated in Table 1. A notable exception is the cadmium 228.802 nm line which is subject to interference from arsenic above the 30 ppm level. Unusually high concentrations of one or more elements in a sample requires a cautious checking for unexpected spectral interferences.

2. Densitometric Analyses

Chromium and cobalt have been used beneficially as internal standards to determine four commonly encountered impurities. For best precision the analytical line pairs shown in Table 3 should be measured with a microphotometer. An internal standard is not used for boron, but its reliability is improved by using the measured transmittances of the lines shown in Table 3.

## Calibration

1. Densitometric Method

Calibrate the emulsion using standard practices. Make quadruplicate exposures of at least four standards. Convert the percent transmittances of the analytical lines and the internal standard lines to log intensity ratios using the emulsion calibration curve. Prepare analytical curves by plotting the log intensity ratio versus the log concentration for each element.

2. Visual Method

Make a single exposure of each standard so that each exposure is adjacent to the preceding one, producing a gradating pattern of element concentrations. Tag the spectral lines indicated in Table 2. Using ink, write the ppm concentrations of each element of the respective standards next to the chosen spectral lines.

3. Standardization Densitometric Method

With each group of samples, analyze two standard samples in quadruplicate. If the averages of control values indicate a curve shift of 20% or more, make one half of the correction needed.

4. Standardization Visual Method

With each group of samples, analyze two control samples in quadruplicate. If the averages of control exceed their established values by 25%, correct all sample values proportionately.

## Calculations

For the densitometric method calculate the log intensity ratio for each analytical line pair from the emulsion calibration curve. Refer this ratio to the previously prepared analytical curve to obtain the percent concentration.

## Precision and Accuracy

For the densitometric method the average coefficient of variation is 14.5 for boron, chromium, iron, magnesium, and nickel in the range of concentrations stated in Table 1. Normally a +100 percent -50 percent

indication of precision is assigned to visual analytical results. For certain elements with sharply differing gradations in spectral responses for adjacent standards, a standard deviation of 30% can be obtained. The accuracy of the method can approach the precision stated above provided that appropriate standards are used. This method has been studied in a co-operative test. Summaries of test data from five laboratories are presented in Tables 4 and 5.

Table 1. Elements and Analytical Ranges

| Element | Concentration Range, ppm | Element | Concentration Range, ppm | Element | Concentration Range, ppm |
|---|---|---|---|---|---|
| Antimony | 1 to 200 | Arsenic | 10 to 200 | Gold | 1 to 100 |
| Beryllium | 1 to 200 | Barium | 10 to 200 | Indium | 1 to 100 |
| Chromium | 1 to 200 | Cesium | 10 to 200 | Manganese | 1 to 100 |
| cobalt | 1 to 200 | Phosphorus | 10 to 200 | Rubidium | 1 to 100 |
| Lead | 1 to 200 | Vanadium | 10 to 200 | Tin | 1 to 100 |
| Nickel | 1 to 200 | Zinc | 10 to 200 | Molybdenum | 2 to 100 |
| Potassium | 1 to 200 | Lithium | 0.5 to 100 | Thallium | 5 to 100 |
| Sodium | 1 to 200 | Magnesium | 0.5 to 100 | Silver | 0.1 to 50 |
| Aluminum | 5 to 200 | Copper | 0.5 to 100 | Cadmium | 0.1 to 10 |
| Iron | 5 to 200 | Bismuth | 1 to 100 | Boron | 0.2 to 10 |
| Silicon | 5 to 200 | Germanium | 1 to 100 | | |

Table 2. Visual Spectral Lines, nm

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Ag | 328.068 | Cd | 228.802 | Li | 670.784 | Rb | 780.023 |
| Ag | 338.289 | Co | 345.351 | Mg | 280.270 | Sb | 259.806 |
| Al | 309.271 | Co | 242.493 | Mg | 279.553 | Sb | 287.792 |
| Al | 308.216 | Cr | 283.563 | Mn | 279.827 | Si | 250.690 |
| As | 234.984 | Cr | 284.335 | Mn | 279.482 | Si | 288.158 |
| As | 278.022 | Cs | 852.110 | Mo | 313.259 | Sn | 317.502 |
| Au | 267.595 | Cu | 324.754 | Mo | 317.035 | Sn | 326.233 |
| Au | 242.795 | Cu | 327.396 | Na | 588.995 | Tl | 276.787 |
| B | 249.773 | Fe | 259.940 | Na | 330.232 | V | 318.540 |
| B | 249.678 | Fe | 278.810 | Ni | 305.082 | V | 318.398 |
| Ba | 493.408 | Ge | 265.118 | Ni | 300.249 | Zn | 334.502 |
| Be | 234.861 | Ge | 265.158 | P | 255.328 | Zn | 328.233 |
| Be | 313.042 | In | 325.609 | P | 255.493 | | |
| Bi | 306.772 | In | 303.936 | Pb | 283.307 | | |
| Bi | 289.798 | K | 766.491 | Pb | 280.200 | | |

Table 3. Analytical Lines Used for Densitometry, nm

| Element and Wavelength | | Internal Standard Element and Wavelength | | | |
|---|---|---|---|---|---|
| B | 249.773 | none | | none | |
| Cr | 283.563 | Co | 304.400 | | |
| Fe | 259.940 | Co | 304.400 | or Cr | 276.259 |
| Mg | 280.270 | Co | 304.400 | or Cr | 276.259 |
| Mn | 279.827 | Co | 304.400 | or Cr | 276.259 |
| Ni | 305.082 | Co | 304.400 | or Cr | 276.259 |

Table 4. Summary of Cooperative Test Results for the Spectrochemical Analysis of $U_3O_8$ for Impurities Determined by the Gallium Oxide Carrier D-C Arc Technique - Densitometric Analyses

| | U-1 | | U-2 | | U-3 | |
|---|---|---|---|---|---|---|
| | Average Value[A] | Average Coeff. of Variation[B] | Average Value[A] | Average Coeff. of Variation[B] | Average Value[A] | Average Coeff. of Variation[B] |
| Boron | 0.87 | 12.7 | 0.38 | 8.7 | 0.57 | 7.5 |
| Chromium | 31 | 16.3 | 7 | 23.1 | 47 | 18.7 |
| Iron | 18 | 20.7 | 119 | 9.4 | 190 | 11 |
| Magnesium | 49 | 21.8 | 6 | 28.9 | -- | -- |
| Maganese | 29 | 8.9 | 8 | 13 | 38 | 10.1 |
| Nickel | -- | -- | 97 | 8.7 | 120 | 12.3 |

[A] Values are µg/g U
[B] The percent coefficient of variation

Table 5. Summary of Cooperative Test Results for the Spectrochemical Analysis of $U_3O_8$ for Impurities Determined by the Gallium Oxide Carrier D-C Arc Technique - Visual Comparative Analyses

| | U-1 | | U-2 | | U-3 | |
|---|---|---|---|---|---|---|
| | Average Value[A] | Average Coeff. of Variation[B] | Average Value[A] | Average Coeff. of Variation[B] | Average Value[A] | Average Coeff. of Variation[B] |
| Aluminum | 62 | 11.6 | 8 | 21.1 | -- | -- |
| Bismuth | 35 | 17.6 | 5 | 19.3 | -- | -- |
| Copper | 2 | 12.2 | 46 | 8.5 | 50 | 5.4 |
| Molybdenum | 35 | 19.4 | 6 | 18.3 | -- | -- |
| Phosphorus | 203 | 13.8 | -- | -- | -- | -- |
| Silicon | -- | -- | 193 | 9.0 | 267 | 6.7 |
| Tin | 27 | 19.9 | 2 | 33.8 | -- | -- |
| Vanadium | 70 | 14.6 | 20 | 16.1 | -- | -- |
| Zinc | -- | -- | 133 | 13.6 | -- | -- |

[A] Values are µg/g U
[B] The percent coefficient of variation

# ANALYSIS OF IMPURITIES IN URANIUM BY INDUCTIVELY COUPLED PLASMA SPECTROSCOPY AFTER SOLVENT EXTRACTION SEPARATION

## Summary of Method

The extraction method described herein is a modified version of a method described by Walker and Vita[1] prior to analysis by Atomic Absorption. The method was applied in conjunction with Inductively Plasma Measurement (ICP) by Maney, Luciano and Ward[2].

The sample of uranium is dissolved in concentrated acid, diluted to volume and the solution is treated with tri-n-butyl phosphate (TBP) to separate the uranium from the impurities. The aqueous solution containing the impurities is analyzed using an ICP spectrometer.

## Equipment and Reagents

Separatory flasks of 60 to 100 mL capacity are required for the extraction procedure. The acids and water used should be of the highest possible purity to optimize the extraction process. The organic reagents used are tri-n-butyl-phosphate (TBP) and carbon tetrachloride and both should be pre-washed with 6N nitric acid even if they are designated as purified materials. The instrument used for the analyses was a Jarrell-Ash Model 975 direct reading ICP spectrometer. The operating parameters and some specifications are listed in Table 1. Any ICP instrument of either the simultaneous or sequential type with comparable or better dispersion could be used. The use of a sequential instrument would of course result in a smaller sample throughout.

## Sample Preparation

A 1-2 g sample of uranium (as oxide or fluoride) is weighed into a 100 mL beaker and digested to fumes in 5 mL of concentrated nitric acid. The residue is dissolved in 20 mL of 6N nitric acid. Transfer the solution to a separatory flash and add 40 mL of TBP. Shake the contents for at least 2 minutes (take care to vent the flask occasionally) and then allow 15 minutes for good separation of the organic and aqueous layers.

The aqueous layer is drawn off and saved in a second separatory flask. Wash the organic layer with 10 mL of 6N nitric acid and combine this wash with the first aqueous solution. The second wash should re-extract any

trace metals that may have been extracted along with the uranium. Add 10 mL of carbon tetrachloride to the combined aqueous solutions and shake the contents to remove any TBP that was drawn off with the aqueous layer.

Transfer the aqueous solution to a 100 mL beaker and heat to near dryness to eliminate the excess acid. Dissolve the residue in 5 mL of 0.2N nitric acid. For the best possible sensitivity the 5 mL of solution can be analyzed directly or preferably it can be diluted to a 25-50 mL volume in 0.2N nitric acid. The sample is now ready for ICP analysis.

## RESULTS AND DISCUSSION

Recoveries for the various trace metals are shown in Table 2. Listed values are the percentages of 5 ppm standard additions remaining after the uranium is extracted. These recoveries are usually reproducible to well within ± 5%. After an average extraction, only 0.01% of uranium remains in the aqueous phase.

Detection limits in ppm for elements in aqueous solutions, both in the presence of 1000 ppm uranium and in a uranium extracted solution are presented in Table 3. These detection limits are defined as the concentration required to give a signal equal to twice the standard deviation of ten consecutive exposures of the various blanks. A distinct similarity is observed between the detection limits in water and the extracted uranium blank. The detection limits in the presence of 100 ppm uranium are markedly degraded because of the larger noise level resulting from the high background.

The degradation of the calcium results by more than a factor of 30 can be explained by the number of uranium lines adjacent to the 317.9 nm calcium line. Cobalt, iron, manganese, and vanadium are other elements whose detection limits suffer in the presence of high concentrations of uranium. Detection limits for these elements worsened by more than a factor of 10 in the presence of a 1000 ppm uranium solution.

Detection limits for metals in the original undissolved sample are presented in Table 4. In order to dissolve a 1 g uranium sample and obtain a 1000 ppm uranium concentration, a dilution factor of 1000 is required. Therefore, the lowest detectable amount in the original sample would be 1000

times higher than the detection limit of the solution. When extractions are performed, however, a large dilution factor is not required to mitigate uranium interference. In this example where a 1 g sample was put in a final sample volume of 5 mL, the calculated detection limits for the original solid sample are only a factor of 5 worse. Extraction processes allow for the improvement of detection limits by using larger sample sizes and smaller final volumes.

Concentrations found in a high purity uranium oxide sample are listed in Table 5. In most cases, it is obvious that ICP sensitivity is capable of determining the concentration of impurities when a 1-5 dilution is involved. In summary, the accuracy and sensitivity of ICP analysis combined with solvent extraction make it a useful technique for the analysis of uranium containing products.

## REFERENCES

[1]C.R. Walker and O.A. Vita, "Determination of Impurities in Uranium Compounds by Atomic Absorption, "Analytica Chimica Acta, 43 (1968) 27, 35.

[2]J.P. Maney, V. Luciano and A.F. Ward "Analysis of Energy Resources by ICAP Spectroscopy Part III: Uranium" Jarrell-Ash Technical Application Note #3.

Table 1. Instrument Specifications

| | |
|---|---|
| Instrument : | Jarrell-Ash Model 975 |
| Focal Curve: | 0.75 m |
| Grating : | 2400 grooves/mm |
| Wavelength Range | 190 to 500 nm in air |
| Linear Dispersion | 0.54 nm/mm in 1st order |
| Gas Flow: Coolant | 18 L/min |
| Plasma | 0 L/min |
| Nebulizer | 0.7 L/min |
| RF Power: Forward | 1100 W |
| Reverse | 10 W |
| Observation Height | 16 mm above working coil |
| Integration Time | 2 x 7 sec on line |
| | 1 x 7 sec on background |
| Nebulizer | Cross flow type |
| Solution Uptake | 1 mL/min° |

Table 2. Recoveries

| | | | |
|---|---|---|---|
| Al | 99% | Mn | 92% |
| As | 79% | Mo | 87% |
| B | 82% | Ni | 89% |
| Ba | 94% | Pb | 89% |
| Cd | 87% | Rh | 94% |
| Co | 92% | Se | 85% |
| Cr | 94% | Sr | 94% |
| Cu | 92% | Ti | 84% |
| Fe | 100% | V | 87% |
| Li | 91% | Zn | 87% |
| Mg | 97% | U | 0.01% |

Table 3. Detection Limits in Solution (ug/L)

| | $H_2O$ | 1000 ppm U | 100% U (extracted) |
|---|---|---|---|
| Ca | 3 | 100 | 22 |
| Co | 1 | 15 | 2 |
| Fe | 1 | 20 | 6 |
| Mg | 0.1 | 1.5 | 4 |
| Mn | 0.5 | 6 | 0.6 |
| Ni | 8 | 14 | 4 |
| Pb | 15 | 25 | 20 |
| Sr | 0.2 | 0.8 | 0.2 |
| Ti | 1 | 5 | 2 |
| V | 2 | 25 | 3 |
| Zn | 1 | 1.5 | 1 |
| Zr | 2 | 15 | 5 |

Table 4. Detection Limits in Original Sample µg/g

| | 1000 ppm U | 100% U (extracted) |
|---|---|---|
| Ca | 100 | 0.11 |
| Co | 15 | 0.01 |
| Fe | 20 | 0.03 |
| Mg | 1.5 | 0.02 |
| Mn | 6 | 0.003 |
| Ni | 14 | 0.02 |
| Pb | 25 | 0.2 |
| Sr | 0.8 | 0.001 |
| Ti | 5 | 0.01 |
| V | 25 | 0.015 |
| Zn | 1.5 | 0.005 |
| Zr | 15 | 0.025 |

Table 5. Typical Analysis of High Purity $U_3O_8$ (µg/g of $U_3O_8$)

| | | | |
|---|---|---|---|
| Al | 1.0 | Mg | 1.75 |
| As | 0.65 | Mn | 0.50 |
| B | 0.34 | Mo | 0.08 |
| Ba | <.01 | Ni | 0.93 |
| Ca | 7.0 | Pb | 0.39 |
| Cd | 0.07 | Rh | <.15 |
| Co | 0.02 | Se | 0.1 |
| Cr | 1.72 | Sr | 0.54 |
| Cu | <.01 | Ti | 0.19 |
| Fe | 7.5 | V | <.01 |
| Li | <.02 | Zn | 0.34 |

# MEASUREMENT OF IMPURITIES IN URANIUM PROCESS SOLUTIONS BY INDUCTIVELY COUPLED PLASMA SPECTROSCOPY

## Summary of Method

Uranium process solutions are diluted sufficiently to reduce the concentration of any alkali ions which can cause enhancement or suppression effects. The impurities in the solutions are then measured directly using an Inductively Coupled Plasma Spectrometer. Results for nine elements are presented but the method can be used to measure any elements for which a suitable wavelength free from uranium or other line interferences can be selected.

## Equipment

The ICP spectrometer must be capable of providing a resolution of 0.006 nm or better as measured at a wavelength in the region of the iron triplet at 310 nm. The instrument must be of the sequential type or have freedom of wavelength choice. The specifications and operating conditions for the instrument used to analyze the process solutions described herein are listed in Table 1.

## Procedure

Process solutions can be measured directly without dilution if the uranium concentration is of the order of 2 to 3 g/L and the salt concentration is 0.1 molar or less. Solutions with higher concentrations must be diluted to avoid effects which can render the results completely unreliable.

Careful selection of a sensitive analytical wavelength for each element to be measured is crucial to the success of the measurements. For each sample the region around selected wavelengths for each element should be examined to ensure that there are no interfering lines. In addition, if the background on either or both sides of the selected lines are high then measurements should be made at these positions so that appropriate corrections can be applied. The wavelengths selected for the nine elements measured in the process solutions used to test this method are listed in Table 2.

To provide suitable calibration data and for subsequent standardization a set of at least two standards for each element must be prepared. Each standard solution can contain some or all of the elements to be measured. The standard solutions can be prepared from high purity compounds or from commercially prepared solutions. If the approximate composition of the matrix of the solutions to be analyzed is known then the standards should be prepared with a similar matrix. Any reagents used must be of the highest possible purity to obtain optimum detection limits. In addition, the reagents should be analyzed to ensure that they are not contributing impurities or to provide data which will allow corrections to be made. The standards used for the analysis reported herein were prepared from commercially available standard solutions using purified nitric acid to provide a 1% acid solution. If a suitable certified reference material is available then a sample of this material should be analyzed as a further verification of the accuracy of the results. During measurement of a set of samples a standard should be included after at least each 5 samples or more often if the spectrometer system is subject to instrumental drift. In addition, the accuracy of wavelength selection should be checked periodically to ensure that the correct wavelength is being measured.

## RESULTS AND DISCUSSION

Measurements for a batch of uranium process solutions are presented in Table 3. The results for uranium were determined by X-Ray Fluorescence and indicate the approximate concentration. All the analytical wavelengths selected (Table 2) were sufficiently resolved from any adjacent wavelengths that it was not necessary to apply any interelement corrections. The reagent blank (nitric acid) contained measurable amounts of Mo and Fe which necessitates a correction for these elements for maximum sensitivity. All results are the average of three determinations and the percent relative standard deviations were typically in the range of 0.5 to 2.5% which indicates a good short term measurement stability. The measurements were also repeated after an interval of a few days and all results agreed within a 0.5 to 5% relative change with the initial set of measurements. A certified reference material was not available to verify the accuracy of the

measurements. An approximate check on the accuracy was achieved by analyzing for the elements Mo, Fe, As and V by both Atomic Absorption and X-Ray Fluorescence techniques. Results of these measurements on two samples are compared with the ICP results in Table 4. While the results indicate that the ICP values for these four elements are probably accurate to within ± 15% of the true value there is no certainty of the absolute accuracy of the results. This serves to emphasize the necessity of a certified reference material to establish the accuracy of measurement.

The major disadvantage of the measurement of solutions without prior separation of uranium is that optimum sensitivity cannot be achieved because of the high backgrounds for many of the elements. The sensitivity is adequate for many routine applications. The detection limits for the solutions measured in this investigation were approximately 0.1 µg/mL for the diluted (1:10) solutions, with the exception of As which is 0.5 µg/mL. The advantage of this method is the reduced number of sample preparation steps which can provide improved precision and higher sample throughout.

Table 1. Specifications and Operating Parameters

| | | |
|---|---|---|
| Instrument | : | Jobin Yvon Model JY 38 |
| Focal length | : | 1 meter |
| Grating | : | 3600 grooves/mm |
| Wavelength Range | : | 170 to 500 nm (Nitrogen purged) |
| Linear dispersion | : | 266 nm/mm in first order |
| Resolution | : | .006 nm (measured at 310 nm) |
| Gas Flow: Auxiliary | : | 0.2 L/min |
| Plasma | : | 16 L/min |
| Nebulizer | : | 0.8L/min |
| RF Power: Forward | : | 1100 watts (27.17 MHz) |
| Reflected | : | 0 watts |
| Integration Time | : | 0.5 s/pt. |
| Nebulizer | : | Meinhard Type |
| Solution Uptake | : | 1.5 L/min |

Table 2. Wavelengths Selected

| Element | Wavelength (nm) |
|---|---|
| Al | 221.005 |
| As | 193.699 |
| Ca | 315.891 |
| Fe | 238.201 |
| Mg | 279.563 |
| Mo | 202.025 |
| Ni | 231.600 |
| V | 214.005 |
| Zr | 256.895 |

Table 3. Process Solution Results (µg/mL)

| Sample | Al | As | Ca | Fe | Mg | Mo | Ni | V | Zr | U (g/L) |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 320 | 1.5 | 175 | 150 | 72.0 | 107 | 0.7 | 80.0 | 29.0 | 21.9 |
| 2 | 300 | <0.4 | 175 | 100 | 57.0 | 30.0 | 0.7 | 60.0 | 3.0 | 22.0 |
| 3 | 275 | <0.4 | 165 | 90.0 | 55.0 | 12.0 | 0.5 | 53.0 | 1.9 | 16.9 |
| 4 | 325 | 7.4 | 139 | 44.0 | 52.0 | 32.0 | 3.0 | 24.0 | 153 | 17.4 |
| 5 | <0.5 | 10.0 | 3.5 | 0.5 | 0.4 | 24.0 | 0.2 | 1.6 | 11 | 19.6 |
| 6 | <0.5 | 4.5 | 2.5 | 0.5 | 0.2 | 15.0 | <0.1 | 3.0 | 5.8 | 12.8 |
| 7 | <0.5 | 4.5 | 2.4 | 0.4 | 0.2 | 22.0 | 0.2 | 2.0 | 6.3 | 21.9 |
| 8 | 246 | 3.5 | 139 | 134 | 24 | 100 | 0.6 | 82.0 | 59.0 | 7.0 |
| 9 | 13.0 | 4.0 | 30 | 75.0 | 3.0 | 12.0 | 0.6 | 62.0 | 3.0 | 10.8 |

Table 4. Technique Comparison (µg/mL)

| Sample | Mo | | | Fe | | | As | | | V | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | XRF | ICP | AAS | XRF | ICP | AAS | XRF | ICP | AAS | XRF | ICP | AAS |
| 9 | 31 | 26 | 32 | 99 | 80 | 89 | 29 | 4 | 5 | 116 | 56 | 66 |
| 10 | <11 | 7 | 8 | 16 | 4 | 4 | 6 | 2 | 3 | <36 | 13 | 15 |